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Advances in Materials Science
Metals and Ceramics Division
Triannual Progress Report
February through May 1980

Scientific Editor: John J. Truhan
General Editor: Kenneth M. Gordon

MASTER

August 1, 1980

**Lawrence
Livermore
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*Materials Engineering Division

[†]Chemical Engineering Division

Advances in Materials Science

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Magnetic fusion energy program*

Superconductor development

Lawrence Livermore Laboratory has sponsored and monitored a superconductor development program in industry since 1974 to ensure that a Nb_3Sn superconductor able to meet the 12-T requirements of future mirror experiments will be available. We are currently working with a commercial supplier to manufacture a Nb_3Sn superconductor for demonstration in the High Field Test Facility (HFTF). Successful operation of the HFTF will provide the experience needed to construct 12-T coils.

The Nb_3Sn superconductor is a strain-sensitive material that requires special handling and process design to prevent degradation of its superconducting properties. Small strains can result in large changes in properties. For example, a compressive strain of about 1% can reversibly halve the critical-current at 12 T, and a tensile strain greater than 0.2% can irreversibly degrade the critical current. Consequently, the successful use of Nb_3Sn in large high-field magnets requires a complete understanding of the mechanical properties of the superconductor.

One superconductor composite currently used consists of filaments of Nb_3Sn in a bronze matrix, and its mechanical behavior is fairly well understood. It is made by the following steps: niobium rods are loaded into holes drilled in a bronze (Cu:13-wt%-Sn) billet, and a nose and cap are welded onto the bronze to form an extrusion billet. This billet is extruded, drawn, and formed into a hexagonal rod. The rod is cut into short lengths and loaded into a second billet, which is extruded and drawn. The resulting rod is clad with a tantalum diffusion barrier and high-purity copper and reduced to wire by cold drawing. The wire is wound into a triplet cable, and six of these are then wound together. The resulting 18-strand cable is jacketed with additional copper, compacted, and formed into a rectangular cross section. This component, called the core, is then heat treated so that the tin from the bronze matrix reacts with the niobium filaments to form the Nb_3Sn superconductor. Finally, embossed copper strips are soldered to each side of the core to produce a fully stabilized conductor.

When the composite is cooled from the heat-treating temperature (typically 900 K) to the operating temperature (4.2 K), the differential thermal contraction between Nb_3Sn and bronze places the Nb_3Sn filaments in compression. If the cooled superconductor is then subjected to tensile stress during handling or fabrication, the critical current increases to a maximum at the point at which the compressive strain has been relieved and subsequently decreases as the Nb_3Sn filaments are placed in tension. The degree of precompression is controlled largely by the ratio of bronze to Nb_3Sn in the conductor.

During the last reporting period, we studied several practical conductors in which precompression resulting from components other than the bronze matrix was important.

HFTF Nb_3Sn superconductor

A cryostable Nb_3Sn conductor designed to operate at 5 kA and 12 T is being manufactured for the HFTF. This conductor consists of a core clad with copper after reaction. The core cross section (Fig. 1) consists of 58% Cu, 30% bronze, 10% Nb_3Sn , and 2% Ta. The copper in the core is annealed during the reaction

*For more information, contact R. M. Scanlan (415-422-7002).

Fig. 1. Transverse section of Nb_3Sn superconductor. This cable was made by wrapping 18 strands of bronze–niobium–filament composite in a copper tube, shaping the tube into a rectangular cross section (4.65×9.47 mm), and then heat-treating this core piece to form Nb_3Sn at the bronze–niobium interfaces.

step and contributes little to the precompression on the Nb_3Sn . The bronze is also annealed during the reaction and is depleted of tin. When these effects are taken into account, the resulting precompression of the Nb_3Sn can be predicted by graphic means and by computer modeling. In addition, the strain–critical-current behavior can be modeled by introducing a strain dependence for the parameters in an empirical expression for critical current. The experimental strain–critical-current behavior of the HFTF core is shown in Fig. 2.

After the Nb_3Sn -forming reaction, additional copper (equal to about 50% of the total cross section) is soldered to the core. This copper has a yield strength of about 300 MPa (Fig. 3); hence, it contributes to the precompression of the Nb_3Sn when the conductor is cooled from the cladding temperature (553 K) to the 4.2-K operating temperature. The calculated value of additional precompression on the Nb_3Sn resulting from differential thermal contraction of the copper strips and Nb_3Sn between 553 and 4.2 K is 0.5%. This precompression occurs in two steps: during the cooling from 553 to 293 K and during cooling from 293 to 4.2 K. The amount of compressive strain actually transmitted to the Nb_3Sn during the first step depends upon experimental conditions (i.e., the extent to which the solder between core and cladding yields during the cladding operation).

This precompression caused by the cladding is useful because it provides greater strain tolerance during coil winding and coil operation. However, the Nb_3Sn critical current is reduced because of the compression, and this fact must be considered in designing the conductor.

Large coil program (LCP) conductor

Another Nb_3Sn -base conductor of practical interest is the forced-flow conductor used in the LCP. Strands of 0.7-mm-diameter multifilamentary Nb–bronze are insulated, cabled, and wrapped in a stainless steel jacket before heat treatment to form Nb_3Sn . The strain–critical-current behavior of the individual strands has been measured, and the results are adequately predicted by an analytical method.¹ To verify the

Fig. 2. Experimental strain-critical-current behavior of the HFTF core. The critical current (normalized to the value for zero applied strain) is plotted as a function of the applied tensile strain for the HFTF core. The change in critical current with applied tensile strain is reversible up to a strain of 0.7%.

behavior of these strands in the final conductor, we prepared a series of samples for testing in the LLNL tensile-testing facility. The samples consisted of 81-strand cables that were compacted in Type 304 stainless steel tubes; about 33% of the cross-sectional area was reserved for helium coolant. The ends of the sample were compacted to form current terminations and pinned to the steel jacket to ensure that the strain was imparted to both the cable and the jacket. Strain gages and voltage taps were placed on the samples in the 5-cm uniform field zone of the test magnet. Figure 4 compares strain-critical-current behavior for these samples with the single-strand data. The initial critical-current values for $H = 8$ T are suppressed to 75% of the single-strand values, and the peak in critical current is shifted from ~ 0.2 to $\sim 0.8\%$ applied strain. Although the strain-critical-current behavior of the single strands and the total conductor are quite different, the critical-current value at the maximum is the same for both cases. To verify that this behavior is caused by the stainless steel jacket, we also tested identical samples with copper jackets (Fig. 4). These critical-current values correlated with the values for the single strands.

The difference in behavior of the stainless steel-jacketed conductor compared to that of the single strands is explained by considering the thermal contraction of the stainless steel jacket as it cools from the reaction temperature (973 K) to 4.2 K. The stainless steel jacket comprises about 47% of the conductor cross section and has a thermal expansion coefficient of $\alpha = 18.7 \times 10^{-6}/\text{K}$. Two properties of stainless steel are important: 1) the differences in thermal-expansion coefficients of stainless steel and Nb_3Sn and of bronze and Nb_3Sn are similar; 2) the higher yield stress of stainless steel compared to that of bronze, especially at higher temperatures, means that the stainless steel applies a compressive strain to the Nb_3Sn much more effectively. If the data appropriate for stainless steel are used to calculate the precompression on the Nb_3Sn , a value of

Fig. 3. Experimental stress-strain data for the HFTF core and HFTF cladding at 4.2 K. The cladding is half-hardened copper that has a yield strength of about 300 MPa. The cladding contributes to the precompression of the Nb_3Sn when the conductor is cooled from the cladding temperature (553 K) to the 4.2-K operating temperature.

0.08% precompressive strain is obtained, which agrees well with the experimental results shown in Fig. 4. This value of precompression is not only greater than that necessary to protect the Nb_3Sn from damage during winding and operation, but the critical current at 12 T is half that of the unstrained case. Consequently, using stainless steel (or work-hardened copper) to provide strength presents a significant design problem to be addressed and overcome in optimizing superconductor operation at 12 T.

Effect of strain on the cubic-to-tetragonal transformation in Nb_3Sn

When Nb_3Sn is cooled below 45 K, it undergoes a martensitic transformation from a cubic to a tetragonal form. We are currently trying to learn if strain affects the temperature of this transformation.

We conducted x-ray diffraction studies in a cryostat cooled with liquid helium. A heater allowed us to vary the temperature from 10 K to well above the transformation temperature. A strain gauge was mounted on the sample, a thin foil of Nb_3Sn , that was, in turn, placed on a vise-like arrangement made of either copper or iridium. This vise could be opened from outside the cryostat to provide the necessary strain on the foil.

We monitored the x-ray diffraction peak height and peak width of the 116 reflection as a function of both strain and temperature. The 116 reflection undergoes an appreciable increase in diffracted intensity and sharpening in width as the cubic-to-tetragonal transformation occurs. Our preliminary results indicated that strain increases both the transformation temperature and the amount of material transformed to the tetragonal form.

Fig. 4. Comparison of strain-critical-current behavior for samples consisting of jacketed 81-strand cables with single-strand data. The peak in critical current is shifted from ~ 0.2 to $\sim 0.8\%$ applied strain. Although the strain-critical-current behavior of the single strands and the total conductor are quite different, the critical-current value at the maximum is the same for both cases. To verify that this shift is caused by the stainless steel jacket, we tested identical 81-strand cables in copper jackets; the critical current values equal the single-strand values.

Rotating-target neutron source II (RTNS-II)

The RTNS-II at LLNL produces an intense neutron flux that is used to study neutron damage in fusion-reactor materials. The target assembly for the RTNS-II (Fig. 5) is coated with tritium-loaded titanium. When a deuteron beam is directed on the target, neutrons are produced by the reaction between deuterons and the tritium. Because this reaction causes intense local heating of the target, rotation and internal water-cooling are used to distribute and remove the heat. The targets used are 23 and 50 cm in diameter. They are rotated at about 5000 rpm, and the stresses on large targets are greater than on the small targets.

We have encountered difficulties in target fabrication, especially the 50-cm-diam targets. After bonding and forming, the 23- and 50-cm-diam targets are pressure-tested by hydraulically pressurizing the internal water channels to 3.5 and 17 MPa, respectively. Although most of the small targets survive the pressure test, most of the large targets fail.

Fig. 5. Target assembly for the RTNS-II. A deuteron beam is directed on the target (which is coated with tritium-loaded titanium), and reaction between deuterons and the tritium produces neutrons. Because this reaction causes intense local heating, the target is rotated at about 5000 rpm to distribute the heat, which is removed by internal water-cooling.

The targets are made as follows:

1. Target blanks are cut to the proper size from sheets of alloy metal, and channels are chemically etched into one of the faying surfaces. Target alloys used to date include Glidcop (copper hardened with an alumina dispersion), Amzirc (precipitated copper hardened with zirconium), and MZC (precipitated copper hardened with magnesium, zirconium, and chromium).
2. Areas not to be bonded are masked.
3. Faying surfaces of Glidcop targets are electrolytically coated with 0.5 mil of copper and 0.25 mil of gold; Amzirc and MZC targets are coated with 0.1 mil of copper and 0.25 mil of gold.
4. Three sets of targets are placed in a stainless steel bonding canister; each set is separated by a stainless steel spacer that helps give uniform pressure transmission.
5. The canisters are evacuated and welded shut using an electron beam. They are hot isostatically pressed at about 510°C and 21 MPa for 1 h.
6. The bonded targets are removed from the canisters and pressure tested.
7. Targets that pass the test are cold formed into the required dish shape and again pressure tested. The forming process often damages the bond sufficiently that the target fails the second testing.
8. The good targets are coated with titanium, and the titanium is loaded with tritium.

During this reporting period, we identified two sources of weak bonds: low bonding temperature, which results in poor adhesion at the gold-gold interface, and unequal diffusion rates of gold and copper during bonding, which results in a plane of voids near the bond (the Kirkendall effect).

Recent production runs made using thermocouples attached to the canisters showed that the canister temperatures lag the furnace-wall temperature by a considerable amount. This lag is greater if a 50-cm-diam canister is included in the load stack because the larger diameter precludes good argon circulation and heat transfer within the autoclave. We previously examined a 50-cm-diam target bonded under these conditions and found that failure occurred at the gold-gold interface.

We have also found that the Kirkendall effect contributes to target failure. We analyzed a 50-cm-diam Glidcop target that passed the 17 MPa pressure test before cold forming but failed at about 12 MPa after cold forming. We examined the bond with optical and scanning electron microscopy, x-ray diffraction, and microprobe analysis, and concluded that:

- The gold-gold bond was sound, and failure did not occur along the original interface.
- The gold and copper had reacted to form a disordered gold-copper phase. Furthermore, a plane of voids, arising because of the Kirkendall effect, had formed between the gold-copper phase and the copper. The voids were larger and more numerous on the flat-plate side of the bond than under the lands because pressure across the lands tends to close voids or prevent their formation. Fracture resulted from ductile tearing along this plane of voids.

We are now examining a 23-cm-diam Glidcop target that failed after cold forming at a pressure of about 14 MPa. Here, too, failure took place along a plane of voids between the gold-copper and copper phases.

We compared the diffusion profiles of gold-copper bonds taken from these targets to determine the equivalent annealing time at 510°C required for proper bonding. We found that formation of a strong bond without voids required annealing for between 15 and 30 min, a time-at-temperature window that would be difficult to achieve in a production process. To avoid this potential production problem, we plan to explore alternate bonding techniques.

Laser fusion energy program*

Damage thresholds of polished glass surfaces

We are working to raise the damage threshold of polished glass surfaces that transmit high-energy laser pulses; such surfaces are more easily damaged than the bulk material. There is speculation that the decreased damage threshold of surfaces results from the polishing process, which may damage the surface and introduce impurities. A previous experiment supports this view: when we exposed a fresh surface of fused silica by fracturing rather than by polishing, we found that the surface had a damage threshold as high as the bulk material.

During this reporting period, we tested the damage threshold of additional polished glass surfaces that had been prepared as part of our polishing studies. Previously, we examined fused silica test pieces that were polished on a nylon lap with 99.9+%-pure CeO_2 and etched with ultrapure hydrofluoric acid; all four tested surfaces showed surface-damage-threshold values above 20 J/cm^2 . We have reproduced this work and verified that these high values can be dependably achieved using a nylon lap. We are currently trying to raise the damage threshold values of fused silica polished using a pitch lap, which is important because we can at present produce optically figured surfaces on pitch laps only.

Among the three types of polished fused-silica glass surfaces tested were samples that had been previously laser damaged. Although these were repolished, we observed damage threshold values below 20 J/cm^2 , which indicated that the effects of laser damage extend more deeply into the surface than we originally suspected. As before, undamaged surfaces gave damage threshold values exceeding 20 J/cm^2 .

We are also extending our investigation to polishing surfaces of BK-7 (a borosilicate glass), which is a much more difficult task because the material surface is chemically active.

Fracturing of laser glass

Since February 1979, we have been looking at freshly fractured laser-glass surfaces as test surfaces to evaluate the effects of contaminants on damage threshold values. Adsorbed gas and surface layers of environmental contamination (such as water) are suspected of lowering damage thresholds.

To date, we have concentrated on fracturing fused silica samples and have developed a mechanical technique: V-notches are made in the glass and a controlled pressure is applied. We also developed a heat technique to fracture BK-7 and fluorophosphate glasses that exploits the coefficients of thermal expansion to fracture the samples.

Our experiments produced surfaces with damage thresholds ranging from less than 13 to more than 50 J/cm^2 . In general, these surfaces were undesirably dusty after fracture. We found that using water (the "wet wick" technique) appeared to minimize this condition, and we are pursuing techniques that use water to prevent the formation of dust or to remove it after fracture. We believe that once the dust problem is eliminated, we will have a very clean surface to use in further studies.

Characterization of platinum-coated microspheres

We have been investigating a batch of platinum-coated glass microspheres, originally intended for use as laser fusion targets, that lost their deuterium-tritium (D-T) fill and were refilled.² The attempted refilling damaged the microspheres badly; the smooth spherical surfaces became blistered and distorted, and scanning electron microscope examination of a cross section showed that the platinum layer, normally dense and quite uniform, was extremely porous and irregular.

During the last reporting period, we completed most of our microstructural and crystallographic study of these microspheres. Because the literature suggested that water formed within the platinum layer, we

*For more information, contact R. L. Landingham (415-422-8022).

evaluated the processing parameters, especially oxygen doping, to determine their effects on the coating structure. We conducted most of our work on flat sputtered platinum films about 5 μm thick. We chose flat films instead of coated balls because of the relative unavailability of microspheres and the inconvenient size and geometry of microspheres for most types of materials testing.

We divided our investigation into three phases. Phase A examined the effect of oxygen on the structure of sputtered platinum film; Phase B examined the effect of the hydrogen filling process on the sputtered-platinum structure; and Phase C addressed the correlation between the structure of platinum films and the actual microsphere coatings. We drew the following conclusions from our experimental results and available literature information:

- Increased oxygen doping in the sputtering stream increased the oxygen content of the platinum coating and resulted in a corresponding expansion of the platinum lattice. No evidence of platinum oxides was found.

- Microstructures of flat sputtered platinum films are not equivalent to those of platinum coatings on spheres. We think that interruptions in the deposition process caused by the motion of the spherical targets produce "bands" or interfaces in the microsphere coatings. Other experimenters have observed similar laminar structures in vapor deposition schemes, but these have not been characterized.³⁻⁶

- Delamination of the platinum coatings on the microspheres appeared to occur along these interfaces. When interfaces were absent, no disruption was seen. However, because interfaces have not been physically, crystallographically, or chemically characterized with respect to the bulk coating, none of the delamination mechanisms that have been proposed can be demonstrated.

Because of the extremely small size and low platinum mass of a single coated microsphere, only Debye-Scherrer and Guinier x-ray techniques successfully produced an x-ray pattern for a single sphere. Neither of these techniques, however, permits the precision of peak-position and peak-shape determinations that are required to assess subtle changes in the platinum structure. Fortunately, a large number of coated microspheres (10^2 – 10^3), known to contain interfaces, have recently become available. We successfully analyzed them using an automated x-ray diffractometer, and, after they are exposed to the high-pressure D-T fill system, we plan to reanalyze them to determine the expected disruption and crystallographic changes that have taken place.

Aluminum-air battery and vehicle research*

The goal of the aluminum-air electric-vehicle project is to develop a commercially feasible general-purpose vehicle that has the range, acceleration, and rapid refueling capability of today's automobile. The aluminum-air power cell currently under study combines an extremely high energy-to-weight ratio with the ability to be refueled by the addition of reactants. By matching the performance of conventional automobiles, the electric vehicle will have the potential for significant market penetration and provide a proportionately large savings of petroleum. We estimate that technical success of the program will allow commercialization in the early 1990's of a vehicle with a purchase price, operating cost, and total energy consumption competitive with advanced automobiles using liquid fuels derived from coal.

The aluminum-air power cell operates as a fuel cell: aluminum plates and tap water are consumed to produce electricity and a reaction product. The reaction product, hydrargillite [$\text{Al}(\text{OH})_3$], is an intermediate produced during the industrial refining of aluminum; it can thus be converted back to the metal without necessitating modification of existing metal-refining technology. During battery discharge, tap water distilled using waste heat serves as the battery reactant and is used to wash the hydrargillite; this washing maintains the hydrargillite product in a highly pure state—a requirement for economical recycling. The hydrargillite is stored as a nonreactive semidry powder that is periodically withdrawn from the vehicle at service stations for subsequent conversion to aluminum plates by the aluminum industry. Thus, a fixed quantity of aluminum provides a reusable energy link between the vehicle and any source of electricity.

A five-passenger vehicle would have a nominal range of 400 km set by the frequency of tap-water additions. Fresh aluminum plates would be added every 1600 to 3200 km, and hydrargillite would be withdrawn every 400 to 800 km.

Major portions of this program are carried out under subcontracts with private laboratories and consulting firms. We at LLNL manage this effort and also maintain a sizable in-house effort in some limited but critical areas. This coordinated program is intended to promote and maintain a high level of scientific and engineering capability in the subcontract research. It is also our responsibility to design the power cell, to foster its commercialization by promoting industrial participation, and to disseminate our results.

The aluminum-air battery sustains three electrochemical and chemical reactions:

The first constitutes the electricity-producing reaction of the cell and typically occurs with a cell voltage exceeding 1.6 V. The reaction produces a supersaturated caustic-aluminate solution. The second reaction is an undesired parasitic consumption of aluminum whose rate is roughly 10% that of Reaction (1); it involves the reduction of water at the aluminum electrode and produces hydrogen gas. For safety, the hydrogen must be effectively disbursed, reacted catalytically, or burned. Thus, it is necessary to drain the electrolyte from the galvanic-cell stack during long periods of standby. Reaction (3) is the precipitation of crystalline hydrargillite, which takes place in a heavily seeded crystallizer unit. The precipitation occurs under conditions similar to those of the decomposition step of the Bayer process, which produces a metallurgical-grade hydrargillite from caustic-aluminate solutions leached from bauxite. The net reaction of the battery [Reactions (1) and (3)] is

This reaction has a theoretical energy value of 8.13 kW·h/kg of aluminum or 2.73 V.

*For more information, contact J. F. Cooper (415-422-7168).

Cell research and development

Our current efforts during this reporting period involved the scale-up of 25- and 50-cm² cells to the full-size 1000-cm² cells anticipated for automotive application. These cells use anodes and cathodes adapted from existing battery, fuel-cell, and chlor-alkali technologies. The cell polarization curves in Fig. 6 were obtained using an alloy containing 0.05% Ga developed for marine applications and an air-cathode developed for chlor-alkali cells. These electrodes were developed for widely differing electrolyte compositions, temperatures, hydrodynamic conditions, and performance objectives, and we discharged them under yet a different set of conditions. The electrodes are therefore not optimized for vehicular use; nonetheless, they provide a tool for large-cell development and a baseline for both vehicular performance projections and for the development of electrodes optimized for this application. The combination of cell-voltage and coulombic-efficiency relationships indicates a broad peak in energy yield in the range between 1 and 2 kA/m² (see Fig. 3 in Ref. 7).

Cathode-polarization curves for three modifications of a carbon-based, platinum-catalyzed electrode are shown in Fig. 7. Polarization losses increased by 150 mV following 312 h of continuous discharge at 1.3 kA/m² in caustic-aluminate at 60°C. The electrodes showed no tendency to deteriorate after 100 h of standby on open circuit in cold, supersaturated caustic-aluminate. We determined this by alternating 1-h periods of polarization at 1.3 kA/m² and 60°C with 24-h periods of standby.⁸ Life testing is planned for electrodes purposely developed for this application.

Fig. 6. Cell polarization curves obtained for a 25-cm² aluminum-air cell that uses an alloy containing 0.05% Ga, which was developed for marine applications, and an air-cathode developed for chlor-alkali cells. The solid and dashed curves show the cell voltage and power density for cells in which the interelectrode separations are 1.5 and 3.2 mm, respectively.

Fig. 7. Cathode-polarization curves for three modifications of a carbon-based, platinum-catalyzed electrode. Polarization losses increased by 150 mV following 312 h of continuous discharge at 1.3 kA/m² in caustic-aluminate at 60°C. The electrodes showed no tendency to deteriorate after 100 h of standby on open circuit in cold, supersaturated caustic-aluminate. The electrolyte compositions were a) and b) 6M NaOH, 1.5M Al(OH)₃, and c) 4M NaOH, 1M Al(OH)₃.

Figure 8 shows the results of the large-scale single-cell tests, which began in April 1980. The cell shown in Fig. 9 was developed at LLNL and tested with a rugged sintered-nickel, silver-catalyzed electrode and an aluminum anode containing 0.07% gallium. These experiments were conducted to determine the behavior of anodes on the large scale and to develop an effective interelectrode separator and methods of air distribution and current collection. At a given current density, the electrode potentials were nearly identical for both the large- and small-scale cells; the wide interelectrode spacer ribs (triangular in cross section with 10% occlusion of the cathode surface) degrade the cell voltage somewhat. Table 1 compares results for the two cells using the air cathode of Fig. 6. The pumping power required to circulate electrolyte and air consumes about 3% of the gross cell output. The aluminum anode dissolves uniformly, even after many hours of cell discharge.

Fig. 8. Results of the large-scale 1000-cm² single-cell tests. The dashed and solid curves represent the 25- and 1000-cm² cells, respectively. Curve a shows the current densities obtained using the air cathode, whose behavior is shown in Fig. 6; Curve b gives the values obtained using a sintered-nickel silver-catalyzed cathode.

Fig. 9. Exploded view of a 1000-cm²-anode aluminum-air research cell developed at LLNL.

Table 1. Performance of small- and large-scale aluminum-air test cells.

Variable	Units	Test cell	
		small	large
Average electrode area	cm ²	24.8	949
Cell voltage	V	1.48	1.42
Anode potential ^a	V	-1.68	-1.65
Cathode potential ^a	V	-1.20	-0.23
Power density	kW/m ²	1.92	1.85

^aMeasured relative to Hg/HgO; the value is uncorrected for IR drop.

Electrolyte composition control

The continuous precipitation of hydrargillite is required to stabilize the electrolyte composition and to produce a reaction product that can be used directly by the aluminum industry. Hydrargillite crystallization also provides a reaction product with a minimum weight and volume and regenerates the sodium hydroxide electrolyte.

In the vehicular crystallizer under development, hydrargillite is formed by Reaction (3). Though extensively studied, the reaction mechanism is not clearly understood, and the literature contains conflicting models and rate data. We therefore, determined the precipitation rate experimentally using batch crystallizers containing 20 wt% seed (area:liquid-volume ratios greater than $15 \text{ m}^2/\text{l}$) and pure caustic-aluminate as well as candidate battery electrolytes containing a stannate corrosion inhibitor. High seed charges and moderately high temperatures ($50\text{--}70^\circ\text{C}$) were chosen to inhibit secondary nucleation. In a vehicular crystallizer, the heavier fraction of the seed bed (particles greater than $40 \mu\text{m}$ in diam) would be preferentially removed, and particle population would be maintained by breakdown of agglomerates or by seed injection.

We added the seed to stirred supersaturated solutions, the temperatures of which were controlled by a water bath, and monitored the concentration decay by measuring the conductivity. The rate equations and constants that we derived from these crystallizer experiments, which were conducted on a scale appropriate to the 1000-cm^2 anodes, confirmed our earlier projections of the mass of seed required for a vehicular crystallizer.

Geothermal research*

The Geothermal Research program at LLNL is aimed at harnessing the total flow of the hot, hypersaline brines available from the Salton Sea field in southern California. A central problem encountered in tapping this enormous geothermal energy resource is that the brine causes scaling and corrosion of turbines, piping, and other equipment. To help minimize this problem, we are studying general corrosion, erosion-assisted corrosion, and stress corrosion of these materials.

Currently, our principal concern is assessing the corrosion resistance of materials in the high-temperature leg of a double-stage flashed-steam electricity-generating system. The materials of interest in the high-temperature leg are the surface piping that leads to the steam-brine separators and the production-well casing. We have two experiments in progress to characterize the corrosion performance of piping and well-casing materials.

Localized corrosion of surface-piping materials

The main concern with piping materials is their susceptibility to localized corrosion. Sections of the 10-in.-diam pipe at the San Diego Gas and Electric Company facility have shown severe attack at elbows and other locations where, presumably, the dislodging of lead sulfide scale exposes the underlying steel to attack. We have observed that alloy steels containing up to 9% chromium and 0.5 to 1% molybdenum suffer much less corrosion in hypersaline brines (including brine that has been acidified to reduce the scaling rate). However, these Cr-Mo alloy steels do suffer some localized attack in the form of shallow pits.

To determine if susceptibility to pitting limits use of these steels in geothermal applications, we attempted to establish the time dependence of this pitting penetration. We began an experiment in June 1979 in which five spools were exposed to geothermal brine and steam; each spool contained four sets of nine commercial carbon- and alloy-steel coupons. The sets of coupons were mounted so that one set was fully immersed in brine, one was partially immersed, and two were exposed to the mist above the brine. Beginning one month after emplacement, one spool was removed each month and analyzed.

The fifth and last spool was removed on January 22, 1980. The general corrosion rate for each coupon was determined by the weight lost during the exposure period (Table 2). The data indicate that the alloy steels were 10 to 20 times more corrosion resistant than the carbon steels; in some cases, even greater resistance was observed. Further, the corrosion rate did not change appreciably with time.

The data in Table 2 were taken from coupons fully immersed in the brine during flow. The wellhead temperature ranged between 210 and 255°C and the pressure between 2.1 and 2.5 MPa. Because the geothermal brine is about 10% liquid, brine flows along the bottom of the pipe and the mist-steam component occupies the upper portion of the pipe. Compared to coupons exposed only to the mist of suspended brine droplets, the immersed coupons were corroded the most severely. During exposure, many pits are nucleated, and these pits grow laterally and coalesce to form bands of attacked metal. All alloys suffer this attack, but the process proceeds most rapidly on the carbon steels. From our observations, we concluded that alloy steels are not likely to fail catastrophically because of pit perforation.

We also measured the thickness of the accumulated scale, which was thickest on the fully immersed coupons. The scale is primarily lead sulfide (PbS), which is semiconducting; because it is porous and brittle, it appears to offer little corrosion protection.

The superior performance of the alloy steels is not easily explained, and we were surprised that an addition of 0.5% of molybdenum should so profoundly reduce the corrosion rate. Further additions of chromium and molybdenum provided only slight improvement in corrosion behavior. We concluded that use of 0.5%-Mo alloy steel (ASTM A204) is cost effective on the basis of the required corrosion allowance, although other factors such as mechanical strength and weldability apply to final materials selection.

*For more information, contact R. D. McCright (415-422-7051).

Table 2. Corrosion rates of coupons exposed at the 6 o'clock position in two-phase wellhead geothermal fluid.

	Corrosion rate (mil/y) after				
	1 month	2 month	3 month	4 month	6 month
Alloy material					
AISI 1010 carbon steel	95	73	82	57	65
ASTM A106 B carbon steel ^a	85	56	67	72	53
0.5 Mo alloy steel ^b	1.4	4.2	0.7	0.5	0.6
1.0 Cr-0.5 Mo alloy steel ^b	1.5	1.9	0.8	0.4	0.6
2.25 Cr-1.0 Mo alloy steel ^b	1.2	2.7	0.7	0.7	0.7
5.5 Cr-0.5 Mo alloy steel ^b	1.3	1.3	0.5	0.4	0.5
9 Cr-1.0 Mo alloy steel ^b	1.5	1.9	0.4	0.4	0.5

^aConstruction material for pipe spools and 10-in. San Diego Gas and Electric Company production line.

^bCommercially available alloy steels (ASTM A204 and A387).

Corrosion of materials for well casings

We recently completed a study of the corrosion performance of well-casing materials. We simultaneously exposed 20 different grades of steel to geothermal well fluid to compare the performance of low- to intermediate-alloy steels with carbon steel. We compared samples of American Petroleum Institute (API) grades of steel, which are used satisfactorily in the less-corrosive environments of oil wells and thus meet only mechanical specifications, to AISI and ASTM alloy steels, which meet strict composition specifications. We also heat treated short lengths of API J-55 and N-80 samples to simulate the different microstructure that might result during fabrication of these steels into tubular products. The heat treatments included austenization followed by air cooling, austenization followed by furnace cooling, spheroidization, and oil quench plus tempering.

A 550-m-long string of 1-1/4-in.-diam pipe samples was prepared. The string consisted of 74 sections, each 6 to 9 m long, arranged so that each of the 20 steel specimens was exposed at different zones of depth in the well. During well operation, the point of flashing varies with the flow rate and moves downward when the brine flow is shut off. (The temperature increases with depth.) Thus, the environment to which the steel specimens were exposed changed with depth and time. During periods of nonoperation, some stratification of chemical species occurs in the stagnant brine; as a result, we believe that the fluid becomes more corrosive at greater depths.

The sections of tubing were joined with J-55 couplings, which introduced a possible galvanic effect between the dissimilar tubes and couplings. However, because of the number of different steels tested, galvanic effects were inevitable regardless of the coupling material, and other materials were unavailable within a reasonable delivery time. Since the J-55 coupling was expected to be sacrificial, the important question became whether the coupling cathodically protected the test material.

The pipe string was emplaced in Magmamax I well for five months, during which period the well flowed about two-thirds of the time. Before the pipe string was withdrawn, a section of J-55 corroded through and about 150 m of the string fell to the bottom of the well; we recovered about 115 m of this section 2-1/2 months later.

Analysis of the corrosion performance of the string is underway. During the last reporting period, we visually inspected each section for perforations and deep penetrations. Generally, corroded areas were easily detected because the voluminous corrosion products had ruptured the lead sulfide scale. These ruptures formed tubercles that apparently continued to grow. The corrosion was nearly always localized. Large areas of surface were covered with scale but intact and free from significant corrosion. Even on the steels that suffered the most severe corrosion attack, most of the surface area remained intact, but where corrosion had begun, attack was extensive.

The API grades of steel (J-55, N-80, and C-75) suffered heavy corrosion in all zones of the well. The corrosion attack resulted in perforations of the tube wall along the length of the tube. In contrast, the compositionally controlled steels (both carbon and alloy) exhibited much less corrosion. Of the alloy steels, the 0.5%-Mo grade consistently showed the poorest corrosion resistance though, of course, the sections were much less corroded than sections of API steels exposed at similar depths. The Cr-Mo alloys showed no significant corrosion-penetration perforations at any depth, including those samples that were recovered from the bottom of the well after nearly eight months of exposure.

Although the galvanic effect between adjacent sections of tubing and J-55 couplings posed an additional concern, we tentatively concluded that the corroding J-55 couplings did not confer much cathodic protection. Hence, the minor corrosion suffered by the alloy steels is truly indicative of their performance.

We are currently analyzing the performance of the samples in greater detail. This analysis consists of selected metallographic sectioning, identification of corrosion products and scale compounds, and quantitative estimates of the galvanic effect.

Nuclear waste management*

Synroc development

The Mineral Waste-Form program is evaluating and working to improve "Synroc" mineral ceramics,⁹ which are proposed as suitable host materials for the long-term storage of nuclear wastes from U. S. defense programs. The Synroc process immobilizes high-level radioactive wastes as dilute solid solutions in the constituent minerals of a synthetic rock made from mixtures of oxides, principally TiO_2 , BaO , ZrO_2 , Al_2O_3 , and CaO .

The program includes the following areas of investigation:

- Study of powder-coprecipitation techniques used to synthesize Synroc systems containing specific radionuclides.
- Phase-equilibrium studies to determine the most thermodynamically stable and leach-resistant mineral-ceramic waste form for the diverse compositions of defense wastes.
- Processing studies to optimize high-temperature fabrication methods for producing phase-equilibrated, high-strength, high-density products suitable for long-term storage.
- Aqueous-leaching studies to determine the behavior of various host minerals and to compare these behaviors with those of other potential waste forms, such as glass. These studies will be conducted both in accelerated modes at high temperature and pressure and in long-term modes.

We have previously described² the preliminary hot-pressing conditions used for Synroc B, Synroc C, and hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$). Synroc B is the basic synthetic-mineral composition without radioactive material; Synroc C is Synroc B combined with 10 wt% simulated commercial nuclear waste,¹⁰ and Synroc D is Synroc B combined with Savannah River defense waste.¹¹ Synroc C and Synroc D differ primarily in their concentration of fission products and actinides, which constitute about 93% of commercial wastes and about 3% of defense wastes (Tables 3 and 4).

Table 3. Synroc C composition.

Oxide	U20	
	wt%	% of total
Synroc additives		
TiO_2	54.3	
CaO	12.4	
Al_2O_3	10.1	
ZrO_2	8.8	
BaO	7.6	
NiO	0.5	
		93.7
Radioactive components		
UO_2	2.7	
Cs_2O	1.5	
SrO	0.7	
Gd_2O_3	0.7	
CeO_2	0.7	
Y_2O_3	0	
Lu_2O_3	0	
		6.3
		100.0

*For more information, contact C. L. Hoenig (415-422-8004).

Table 4. Synroc D compositions.

Oxide	Savannah River waste		U17		S02	
	wt%	% of total	wt%	% of total	wt%	% of total
Nonradioactive components						
Fe ₃ O ₄	38.0		25.8		35.2	
Al ₂ O ₃	32.0		21.5		23.1	
MnO	9.2		6.2		8.0	
NiO	5.1		3.4		4.3	
CaO	3.0		2.0		2.4	
Na ₂ O	6.2		3.8		0	
SiO ₂	1.0		0.6		0	
		94.5		63.3		73.0
Radioactive components						
UO ₂	3.5		2.3		0	
Cs ₂ O	2.0 ^a		0.7		1.2	
SrO			0.7		0.6	
Gd ₂ O ₃			0.7		0.6	
CeO ₂			0.7		0.6	
		5.5		5.1		3.0
Synroc additives						
TiO ₂	0		15.1		14.5	
CaO	0		4.9		4.2	
ZrO ₂	0		4.0		3.2	
BaO	0		0		2.1	
SiO ₂	0		7.5		0	
		0		31.6		24.0
		100.0		100.0		100.0

^aFission products and actinides.

During this reporting period, we tried to reduce the amount of pseudobrookite (Al₂TiO₅) that formed during the urea coprecipitation of Synroc C composition U04.² Our analysis of Batch U04 showed the presence of a substantial amount of pseudobrookite in addition to the basic Synroc minerals (zirconolite, CaZrTi₂O₇; perovskite, CaTiO₃; and hollandite, BaAl₂Ti₆O₁₆). Electron microprobe analysis indicated that none of the simulated radwaste had partitioned into this pseudobrookite phase. In preparing the experimental batch U20 (Table 4), we decreased the concentrations of TiO₂ and Al₂O₃ slightly and increased the BaO content from 3.5 to 7.6 wt%. This composition was hot pressed at 1373 and 1473 K and 27.6 MPa to greater than 95% of the theoretical density in 5 to 20 min; a density approaching 90% was achieved by pressing at 1273 K and 27.6 MPa for about 3 h. X-ray and scanning electron microprobe analyses showed that these modifications of the composition did reduce the amount of pseudobrookite formed.

We also addressed the fact that Savannah River waste contains 6.2 wt% Na₂O, which significantly affects the Synroc D mineral formulation because only a small amount of Na₂O can be accommodated by hollandite. We therefore prepared U17 (Table 4) in which we tried substituting the mineral nepheline (NaAlSiO₄) for hollandite to stabilize the Na₂O. Like hollandite, nepheline is also capable of forming a solid solution with cesium. We were able to form nepheline with no apparent free Na₂O.

In another set of experiments, we compared two processes for preparing Synroc D compositions. Our ultimate goal was to achieve the greatest densification at the lowest temperature and pressure possible; success will have a significant beneficial impact on the expense and degree of complexity in processing large amounts of defense waste under hot-cell conditions. The first process involves coprecipitation of metal salts dissolved in urea and decomposition of the salts to their oxides by calcination in air. The second process (spray drying) involves centrifugally dispersing a slurry of hydroxides, oxides, and water-soluble salts into a heated carrier gas and drying at about 150°C, which is well below the decomposition temperatures of some of the nitrate and hydroxide starting materials.

We used both processing methods to obtain maximum homogeneity and intimate mixing of the starting materials. We encountered difficulty in finding a titanium salt that was soluble in urea; titanyl nitrate decomposed to finely divided TiO_2 , which is insoluble. The nitrate salts of all other cations, however, dissolved satisfactorily in urea.

We also compared the hot-pressing behavior of precalcined and uncalcined powders: U17 and S02, respectively (Table 4). (We assumed that substitution of nepheline for hollandite in U17 would not significantly affect the densification behavior.) Batch U17 was calcined and then hot pressed (Fig. 10). Batch S02 was pressure-reaction sintered, a one-step process in which the oxides are decomposed *in situ* during hot pressing; weight losses as great as 23% were encountered (Fig. 11). Figure 10 shows that for U17, densities greater than 90 to 95% of the theoretical density were achieved; Fig. 10 also shows that densification approaching 90% theoretical could be reached at 1173 K. Comparison of U17 and S02 at 1323 K (Fig. 11) indicates that high-surface-area S02 powders produced *in situ* during thermal decomposition were hot pressed at slightly lower temperatures and pressures.

Table 5 lists the powder properties of Batches U20, U17, and S02.

Fig. 10. Density of Batch U17 as a function of pressure-reaction-sintering time at 1323 K. The hot pressing was carried out at three different pressures.

Fig. 11. Density of Batch S02 as a function of pressure-reaction-sintering time at 27.6 MPa. The hot pressing was carried out at three different temperatures. The densification data for Batch U17 at 1373 and 27.6 MPa is included for comparison.

Table 5. Powder properties of U20, U17, and S02.

Powder	Calcination		Spray drying temperature (°C)	Surface/mass ratio (m ² /g)	Density g/cm ³
	temperature (°C)	duration (h)			
U20	700	66		12.9	4.23
U17	700	56		20.3	3.68
S02			115	155.3	3.71

Phase equilibrium studies of Synroc

During the last reporting period, we used the high-temperature diffractometer to investigate phase formation in Synroc as a function of temperature. An acetone slurry of the U19 powder starting material was placed on a platinum heater and the acetone allowed to evaporate. The temperature was monitored using a Pt-Pt:10-wt%-Rh thermocouple spot-welded to the bottom surface of the heater.

We made diffraction scans at 25, 700, 800, 900, 1000, and 1100°C. The sample was heated to each temperature and allowed to equilibrate for 30 min before the scan was begun. Each scan took about 30 min, which meant that the sample was at the experimental temperature for about 1 h.

Our results indicated that it is possible to form Synroc from a loose powder using these heating schedules, which we found highly encouraging. The order of phase formation seemed to be perovskite, then zirconolite, and then hollandite. The presence of the perovskite and zirconolite phases was initially indicated by broad halos in the diffraction patterns; hollandite was also present, but it was fully crystalline and did not produce these broad halos.

We did not obtain a strong crystalline pattern of a pyrochlore-like phase when we used the U19 powder as a starting material. Instead, this powder initially gave a strong rutile pattern. It appears, therefore, that the pyrochlore-like phase results only when the starting material is fine-grained and homogeneous.

We also continued our investigation of the detailed phase equilibria of Synroc as functions of calcination temperature, hot-pressing parameters (e.g., temperature, pressure, duration), composition, and starting conditions. X-ray intensities of the strongest diffraction line of the different Synroc phases were recorded as a function of calcination temperature and time. Of particular interest was our observation that when cesium was present, the assemblage also went through a pyrochlore-like precursor; this behavior was similar to material calcined at 700°C before it was transformed to Synroc B at higher temperature.² Furthermore, the pyrochlore phase seemed reasonably stable to prolonged heating at 700 and 800°C; above 900°C, it decomposed to give the constituent Synroc minerals and free rutile. We do not yet know which phase gave up the rutile.

Leaching studies of Synroc

We also completed x-ray diffraction analyses on three samples of powder that had undergone accelerated hydrothermal leaching tests at 100 MPa. These samples were prepared by calcining, hot pressing, and sintering at 1325°C for 6 h and were leached in distilled water at 150°C for 10 d, 300°C for 30 d, and 450°C for 13 d.

Comparison with unleached samples showed that materials leached at 150 and 300°C were essentially unchanged. The 450°C sample showed a marked decrease of hollandite and an increase of rutile. We also observed a small amount of non-Synroc minerals in the original preparation, one of which was retained throughout leaching and one of which disappeared during the 450°C run. We concluded that 1) Ba-hollandite was altered during leaching at 450°C, 2) the chemical data obtained from the leachant (distilled water) may reflect the presence of some species that arose from non-Synroc minerals, and 3) some changes may occur in the solid state that are not indicated by chemical analysis of the leachant.

Uptake by plants of radioactive waste materials from contaminated soil

Certain transuranic isotopes present in radioactive waste from nuclear reactors are highly toxic and have long half-lives, which requires that they be isolated from the environment for long periods of time to prevent them from entering man's food chain. One possible pathway by which these materials can enter the food chain involves plant uptake from contaminated soil.

Our research program is investigating the uptake of ²³⁷Np, ²³⁸Pu, ^{239,240}Pu, ²⁴¹Am, and ²⁴⁴Cm by wheat plants. Factors that may influence uptake rates include soil properties (e.g., cation-exchange capacity, soil pH, organic matter content) and the chemical and physical form of the radioisotope in the soil. We studied eight different soils: five from California and three from other states. Four uptake experiments were run, one of which has now been completed.

This study is a cooperative effort with the University of California at Los Angeles and Los Alamos Scientific Laboratory; it is partially funded by the Nuclear Regulatory Commission.

The primary objective of the completed part of the study was to investigate the pot-to-pot variability of uptake of ^{237}Np , ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Am , and ^{244}Cm by wheat plants. Soil from Yolo, California, was uniformly contaminated with the nitrate salts of these radioisotopes and divided among 25 plant containers. A crop of wheat was grown to maturity, and the harvested plants were divided into three components: heads, upper-stem vegetation, and lower-stem vegetation; the heads were further divided into grain and chaff.

The different plant parts were radioassayed using the procedure developed at the University of California at Berkeley. Analysis of the coefficients of variation indicated that more than half of the variability encountered was experimental and somewhat less than half was attributable to analytical variability. We felt that our reproducibility (and variability) was well within the limits needed for meaningful investigations of plant uptake and translocation of transuranic elements.

Neptunium uptake

Analysis of the four plant parts showed that 49.7% of the total neptunium taken up by the wheat plants resided in the lower-stem vegetation; 0.67% was found in the grain.

Plutonium uptake

Analysis of the four plant parts showed that 54.6% of the total plutonium incorporated into the wheat plants was found in the lower-stem vegetation; 0.07% was found in the grain. We observed no significant difference in total uptake or translocation through the plant between ^{238}Pu and $^{239,240}\text{Pu}$. Apparently, wheat plants cannot distinguish among the three isotopes.

Americium and curium uptake

Analysis of the four plant parts showed that 53.2% of the americium and curium taken up by the wheat plants was located in the lower-stem vegetation; 0.29% was found in the grain. Both the total uptake and translocation of these two isotopes through the plant were identical within experimental error. The result was not unexpected since the solution chemistry of these two elements is very similar. Indeed, ^{243}Am is often used as a tracer for ^{244}Cm in yield determinations.

Concentration ratios

We found that wheat plants take up 100 times more Np than Pu, Am, or Cm. Neptunium is also translocated upward through the plant more readily. We also observed that although Pu is more readily taken up than Am or Cm, it is less readily translocated to the grain. This means that translocation to the edible parts of plants must be considered in addition to the root uptake. Many of the literature data do not give the proportions of these isotopes in the edible plant parts, which could make the literature values very misleading. Hence, because there is 1000 times less plutonium in the grain than in the rest of the plant, concentration ratios of 10^{-3} and 10^{-4} reported in the literature are equivalent to ratios of 10^{-6} and 10^{-7} in the grain.

Office of Basic Energy Sciences (OBES) research

Hot corrosion project*

Quantitative models of hot corrosion

The hot-corrosion project is devoted to developing or extending current quantitative models of hot corrosion, which is defined as high-temperature attack of metals exposed to a multi-oxidant system. Hot corrosion is usually associated with sulfidation and molten-salt attack, and it is observed in gas turbines and coal-conversion systems. We are studying pure metals and binary alloys in simple controlled environments to develop a detailed theoretical model of the attack. We have used two major experimental techniques to date: thermogravimetric analysis (TGA) and electrochemical polarization in molten salts. To aid in the development of quantitative hot-corrosion models, we are also determining the thermodynamic properties of chromium sulfide phases important in the corrosion process.

During this reporting period, we concentrated our efforts on making and processing Ni-Cr and Ni-Al binary alloys needed to extend our hot-corrosion study. These alloys will be used to systematically study the effect of composition on anodic polarization when molten Na_2SO_4 serves as the electrolyte. We intend to correlate these results to thermogravimetric analysis of salt-coated alloys to determine the sensitivity and usefulness of electrochemical polarization as a screening technique.

We chose to begin work with the Ni-Cr system for several reasons: 1) it is a relatively simple eutectic system (Fig. 12), and there are no intermetallic compounds that make thermomechanical processing difficult; 2) a substantial amount of chromium dissolves in nickel before a phase change occurs, which means we can add chromium over a wide range of compositions while maintaining a constant microstructure; and 3) the Ni-Cr system serves as the basis of many commercial high-temperature oxidation-resistant alloys that are known to behave well in hot corrosive environments.

We cast alloys with compositions ranging from Ni:2-wt%-Cr to Ni:50-wt%-Cr. After measuring the proper ratio, the elemental components were arc-melted into 100-g ingots four to five times to ensure complete homogenization. These ingots were then sandblasted to remove traces of copper picked up from the crucible and cleaned ultrasonically in solvent before arc-casting into rods about 8 cm long and 13 mm in diameter. A nonconsumable tungsten electrode was used in a 0.5-atm argon environment for both operations. The unused portions of the ingots were cleaned as described and reused for subsequent castings. Casting development was carried out on IN200 because this alloy was readily available.

Sectioning the test castings showed that the top third of the rod (the last to solidify) was more porous than other sections. This porosity can be minimized by preheating the mold or simply recasting the section. Metallographic examination of the cast structure showed that the grain morphology was that expected for a casting of this geometry (Fig. 13). This examination also showed an even distribution of micropores throughout the sample. The pores were about 2 to 5 μm in diameter and separated by 100 to 200 μm ; occasional larger pores (about 10 μm in diam) were also visible.

A slightly higher density of pores existed at the longitudinal axis of the rods. Electron microprobe also showed little coring on a macroscopic scale. The slight loss of chromium from the nominal composition of the alloy probably resulted from the relatively high vapor pressure of chromium; however, remelting the alloy several times did not contribute to this effect. In practice, we are more interested in knowing the final composition than in maintaining the nominal composition.

After casting, the samples were machined to 12 mm in diameter to remove surface defects. We then swaged the samples to 11 mm in diameter, which reduced the cross-sectional area by about 13%. The rods were cold worked so that they could be subsequently recrystallized to produce very large grains. By heat treating, we hoped to eliminate grain size as an experimental variable. A similar procedure was successfully carried out for the pure nickel samples studied previously.¹² We are currently vacuum heat-treating specimens to determine a thermal cycle that produces the desired microstructure.

*For more information, contact J. J. Truhan (415-422-6925).

Fig. 12. Phase diagram for chromium-nickel mixtures. The double-headed arrow indicates the range of alloy compositions that we are currently casting.

Figure 14 shows the large grains that resulted from swaging and heat treating the rods at 1200°C for 30 minutes. The largest grains are almost half the diameter of the sample, but a number of smaller grains still exist, indicating that long exposures will be necessary to eliminate the smaller grains. An alternate method to increase the grain size is to minimize the cold working that precedes heat treating in order to reduce the number of nucleation sites for new grains. We are currently exploring both possibilities.

Fig. 13. Transverse section of sample of Ni:15-wt%-Cr showing grain structure after casting. The metallograph shows an even distribution of micropores throughout the sample.

Fig. 14. Grain growth resulting from swaging and heat treating rods at 1200°C for 30 minutes. The largest grains are almost half the diameter of the sample, but a number of smaller grains still exist, which indicates that long exposures will be necessary to eliminate the smaller grains.

Thermodynamics of sulfides in hot corrosion

The corrosion of metals and metal alloys by sulfidation produces undesirable effects in many of the high-temperature processes involved in energy conversion. High-chromium-iron and high-chromium-nickel alloys promise the best resistance to sulfidation, although relatively little thermodynamic information is available to develop these alloys. To provide protection from sulfur attack, we need to understand the sulfidation process and, in particular, the role played by chromium. We especially need data on the thermodynamics of chromium sulfide formation in order to calculate the driving force for diffusional transport, to develop equilibrium diagrams, and to understand the reaction mechanisms.

Our goals are to determine the equilibrium sulfide phases in Fe-Ni-Cr-Al-S systems, measure the thermodynamic properties of key phases, and calculate the phase behavior as a function of gas and alloy compositions.

During this last reporting period, we began preparing chromium sulfides for calorimetry experiments. Using an arrangement similar to that used by Nishida (Fig. 15),¹³ we prepared more than 100 g of $\text{Cr}_2\text{S}_3(\text{rh})$. Powdered chromium metal was loaded into two small tubes in the hot reaction zone (1273 K) of a sealed quartz tube. Powdered sulfur present in the cool end (673 K) of the quartz tube vaporized and reacted with the chromium to produce the desired sulfide in about 72 h. X-ray diffraction invariably showed that the product was $\text{Cr}_2\text{S}_3(\text{rh})$.

We intend to use part of this Cr_2S_3 to prepare the lower sulfides. The Cr_2S_3 is mixed with the appropriate amount of chromium powder to form the desired sulfide phase. The mixture is then heated at 1273 K in a sealed quartz tube. After 24 h, the tube is opened, and the contents are ground, mixed, and sealed in another tube for an additional 24-h heat treatment at 1273 K. Analysis from our first attempt to prepare Cr_3S_4 has not yet been completed.

We also designed the calorimetry capsules to be used in the chromium sulfide work. A compatibility test showed that platinum reacts with sulfur vapor (which is formed from Cr_2S_3 at 1273 K), despite our initial information that indicated platinum could resist the corrosive action of hot chromium sulfides. We therefore decided to use a quartz capsule contained inside a platinum capsule, which in turn serves as back-up container if the quartz capsule breaks. Even though platinum is not satisfactory for a direct containment vessel, it is the most resistant metal available for secondary containment.

Fig. 15. Three-zone furnace that allows independent temperature control for preparation of chromium sulfides. By adjusting the temperature of the sulfur, the proper sulfur vapor pressure is produced to give the desired chromium sulfide from chromium powder contained in the hotter reaction zones. Use of two hot zones permits double-batch preparation.

Thermochemical cycles for hydrogen production*

We are developing thermochemical cycles to produce hydrogen from water. Hydrogen generated by such cycles would be a renewable resource independent of fossil fuels and could use heat from such energy sources as high-temperature gas-cooled fission reactors, magnetic-fusion reactors, or solar concentrators. We are directing our effort on a detailed study of chemistry of the ZnSe cycle. Our objective is to develop a basic understanding of the thermochemistry, kinetics, and mechanisms of several complex reactions in the cycle.

The thermochemical cycle under study consists of a series of chemical reactions operated in a closed loop so that the only inputs are water and heat and the outputs are separate streams of hydrogen and oxygen. All other chemical reagents are recycled within the system. The major reaction steps in the cycle are:

We are currently studying Reaction (8).

As one alternative to the ZnSe cycle, we are also studying the LiH cycle described by Behr *et al.*¹⁴ This hybrid cycle combines electrochemical and thermochemical steps and involves the following reactions:

We are developing an electrolyte-membrane system for Reactions 10 through 12.

Decomposition of zinc sulfate

Zinc sulfate is decomposed in the ZnSe thermochemical cycle to liberate oxygen and to regenerate SO₂ as a reducing agent. This is the most endothermic step in the reaction scheme and requires temperatures of about 1200 K. Even at these high temperatures, the reaction is hindered kinetically, and produces SO₃ rather than the thermodynamically favored SO₂-O₂ gas mixture. These characteristics indicate that the decomposition reaction is complex and that it will require effort to optimize decomposition.

*For more information, contact O. Krikorian (415-422-8076).

Our first emphasis in studying ZnSO_4 decomposition was to establish the thermodynamic equilibria of the compounds involved. We were unable to determine the high-temperature properties of ZnSO_4 from literature sources because the heat and mass-transfer characteristics of previous experimental designs were limited. Also, formation of an oxysulfate ($\text{ZnO} \cdot 2\text{ZnSO}_4$) and a phase transformation of ZnSO_4 at 1015 K cast additional doubt on the validity of extrapolations from lower-temperature data. To obtain our own data, we are using drop calorimetry to measure the high-temperature enthalpies of ZnSO_4 and $\text{ZnO} \cdot 2\text{ZnSO}_4$ and the enthalpy of the ZnSO_4 α -to- β phase transition.

During this reporting period, we completed these calorimetry experiments on ZnSO_4 . The ZnSO_4 phase transition appeared to occur over a broad temperature range between 1000 and 1030 K. We could not determine a clear transition temperature despite equilibrium times of more than 15 h. We thus used 1015 K as the transition temperature to calculate a transformation enthalpy for ZnSO_4 of 20.4 kJ/mol at 1015 K.

We can combine these reaction heat capacities with the decomposition pressure data published by Ingraham and Kellogg¹⁵ to derive the heats of reaction and entropies for the decomposition of α ZnSO_4 and $\text{ZnO} \cdot 2\text{ZnSO}_4$. These values, in conjunction with the heats of formation and standard entropies for ZnO and SO_3 , can be used to calculate the heats of formation for α ZnSO_4 and $\text{ZnO} \cdot 2\text{ZnSO}_4$. The agreement of our calculated values with previously published data establishes the validity of our calorimetry measurements.

LiH hybrid cycle

Previous experiments on the LiH hybrid cycle¹⁴ were based on an electrolytic cell using a fused NaOH-based electrolyte operating at 600 to 700 K. Atomic hydrogen forms at the cathode membrane, diffuses through the membrane, and reacts with molten lithium on the other side to form lithium hydride, which remains in solution. The hydrogen can be recovered at higher temperatures using conditions under which the lithium is not significantly volatile. The most serious problem in this cycle is attack by the electrolyte of the metal membrane that separates the electrolyte from the molten lithium. We believe that a nearly neutral or even acidic electrolyte would be more compatible with cathode-membrane materials. We plan to investigate this approach using a mixed metaboric acid-metal borate electrolyte in conjunction with a niobium cathode membrane. Niobium forms an acidic oxide and also serves as an excellent medium for hydrogen diffusion.

This reporting period, we designed and constructed two electrolytic cells. Figure 16 shows one of these cells, which was based on the design used by Behr *et al.*¹⁴ The second cell was designed for the testing of a variety of smaller membranes. It features a stainless steel tube support that allows interchanging a variety of cathode-membrane materials. This combination of cells will allow us to relate the behavior of various smaller membranes to that described in Behr's work.

We also began testing the behavior of our proposed electrolyte. We heated boric acid crystals in a stainless steel beaker to 650 K on a hot plate. The sample melted at about 500 K, which indicated that enough water had been lost during the slow heating to form HBO_2 . The initial melt then became somewhat frothy as additional water was driven off; within 15 minutes of melting, enough water had been removed to form a very viscous melt that formed a glass on cooling. The frothing limits the maximum temperature of a simple HBO_2 - B_2O_3 solution to about 525 K, but if an additive can be found that reduces the viscosity enough to permit steam escape without frothing, higher electrolyte temperatures may be possible.

Fig. 16. The LiH electrolysis cell, which features a tube-membrane cathode that contains molten lithium. Hydrogen formed at the cathode diffuses through the membrane to form LiH.

Optical materials with reduced nonlinear effects*

The development of high-power lasers, principally for fusion research, places increasingly stringent requirements on the properties of transparent optical materials. The electrical fields associated with such laser beams are so intense that higher-order, nonlinear terms in the polarizability of the material become important. This program studies the effects of these nonlinear terms and searches for ways to circumvent or surmount the problems they cause.

One of the effects of interest is self-focusing by nonlinear contributions to the refractive index of a glass. Because fluoride glasses have small predicted nonlinear-index coefficients, they are the most promising candidates for both passive components (such as lenses and windows) and active components (such as the laser-amplifier and Faraday-rotation media) in high-power lasers. Our part in this effort is preparation and characterization of beryllium-based glasses and crystals.

During the last four months, we completed initial crystal-growing experiments using our state-of-the-art equipment. For the first run, we chose to grow chrysoberyl doped with 0.1 wt% Cr_2O_3 by the Kyropoulos method. Unfortunately, the seed crystal was lost, and numerous crystals nucleated at the alumina seed holder to produce several very large chrysoberyl crystals up to 2.5 cm long.

A sample of crystalline BeF_2 , produced by hot pressing powdered BeF_2 glass and isomorphous with α quartz, was cut and polished for optical reflectivity measurements at the Naval Research Laboratory (Washington, DC) to determine the band edge.

We are planning to try growing crystals of AlF_3 . According to the literature, single crystals of cubic AlF_3 have been grown using molten PbCl_2 as a solvent.¹⁶ These crystals were obtained as cubic pseudomorphs as a result of the cubic-to-hexagonal transition at 453°C. We intend to use lower-melting molten-salt solvents that have growth-temperature ranges below 453°C (e.g., PbCl_2 - SnCl_2 and PbCl_2 - ZnCl_2).

Fluorescence-line narrowing of amorphous solids†

We are investigating local structure and interactions in glasses by applying laser techniques for fluorescence-line narrowing. This project has both experimental and theoretical parts. Theoretically, we model glass structures using computer codes; experimentally, we measure the fluorescence-line-narrowing spectra. In addition, we compute the optical properties of the rare-earth ion in our simulated glass. This investigation is nearly complete for the Eu-doped BeF_2 glass.

During the last reporting period, we wrote computer programs using the molecular dynamics technique to simulate rare-earth-doped BeF_2 and alkali beryllate glasses. The molecular dynamics technique computes the motion of ions in phase space by integrating Newton's equations of motion numerically. The temperature is fixed by first giving the ions a Maxwellian velocity distribution. The code then calculates average velocities over the covered phase space.

The molecular dynamics approach offers two advantages over Monte Carlo methods: time-dependent properties can be determined and a faster equilibration is usually obtained in a given amount of computing time.

Rapidly quenched materials**

Very rapid cooling of metallic alloys produces "metallic glasses" that have unique physical and chemical properties not possessed by the corresponding crystalline forms. These amorphous solids are prepared by quenching compositions near the eutectic composition at very rapid rates (10^5 - 10^6 K/s) to suppress the nucleation and growth of the crystalline phase.

*For more information, contact C. F. Cline (415-422-8021).

†For more information, contact S. A. Brawer (415-422-8094).

**For more information, contact J. B. Holt (415-422-8003).

We have been interested in making high-specific-strength (σ_y/ρ) materials, and because of the low density and relative high strength of beryllium, it is an obvious choice as a constituent in any high-specific-strength alloy. Our past work has concentrated on the synthesis of amorphous or "glassy" beryllium-containing binary and ternary alloys. During this last reporting period, our work included formation of extended solid solutions of beryllium alloys and new metastable crystalline phases.

Pure beryllium metal transforms from the common α (hcp) phase to the β (bcc) structure at about 1250°C, which is 27°C below the melting point. Much of the brittleness of α -phase beryllium is attributed to the difficulty of slip along certain planes in the anisotropic (hcp) structure. If a process could be developed to retain the β structure at room temperature, there should be significant improvement in ductility and possible enhancement of other physical properties (e.g., an increase in the critical temperature for superconductivity).

During the last reporting period, we demonstrated that we could retain the β -beryllium structure at room temperature. To our knowledge, this is the first time this has been achieved.

Equilibrium phase diagrams show that addition of certain transition metals to beryllium enlarges the β field at high temperatures and lowers the α - β transition temperature. Nickel lowers the α - β transition temperature to 1065°C, the lowest of any of the alloying elements. We prepared samples of different compositions grouped around the beryllium-rich nickel eutectoid composition. Samples were arc-melted in an oxygen-free argon atmosphere and quenched rapidly using the arc-hammer. X-ray diffraction analysis of the resulting thin foils revealed that the alloy $\text{Be}_{91.8}\text{Ni}_{8.2}$ had retained the β -beryllium structure at room temperature. Several x-ray scans made over a two-month period attested to the stability of the β -beryllium structure at room temperature.

Stabilization of the β structure appears to be a very sensitive function of the nickel content. Alloys containing less nickel were primarily α phase, and the $\text{Be}_{91}\text{Ni}_9$ foil showed the emergence of a " γ " phase, which is a new metastable solid. These findings should permit a full investigation of the physical properties of the β (bcc) phase of beryllium.

During this reporting period, we also investigated the extension of solid solubility of beryllium in aluminum by rapid-quench techniques. Aluminum alloys are useful materials for structural applications, and numerous metals have some degree of equilibrium solubility in aluminum. One of the most exciting new aluminum alloys is Al-Li, which offers relatively high strength, high elastic modulus, and low density; yet Al-Be, which should be stronger and more elastic than Al-Li, has received very little attention. Although phase diagrams indicate that the solubility of beryllium in aluminum at 600°C is very low (0.07–0.10 at.%), we were able to extend this to 10 at.% at room temperature by rapid quenching with the arc-hammer. X-ray analysis of each sample foil (aluminum containing from 1 to 15 at.% beryllium) showed only the α -Al (fcc) phase, which indicated the extended solid solution of the beryllium. Our extension of the solid solubility of beryllium in aluminum raises the possibility that a new Al-Be alloy with attractive mechanical properties can be developed.

There is evidence from other studies, however, that such highly extended solid solutions are subject to solute clustering during quenching from the solid state. If the lattice constant is plotted as a function of composition, the constant decreases as beryllium is added to the aluminum until a concentration of 5 at.% Be is reached. Above that amount of added beryllium, the constant again rises to about the value of the 1-at.%-Be sample. This behavior is consistent with the Vickers hardness value, which increases from 38 kg/mm² for pure aluminum to about 200 kg/mm² for Al:5-at.%-Be and then decreases. On the basis of these data, we could conclude that clustering occurs in compositions containing more than 5 at.% Be. We have submitted samples of our foils for electron microscope examination to determine the amount of clustering that may have taken place. We are also measuring the mechanical properties of quenched and quenched-and-annealed foils to assess their technological importance.

Chemistry and Materials Science research

Metallic-alloy glasses*

We are producing new materials, mainly alloy glasses, using rapid-quenching techniques and determining their properties. The general direction of our research is guided by potential applications of these materials in the Nuclear Explosives Program.

During this quarter, we successfully melt-spun a high-strength Mo-Ru-B-based alloy as a high-quality ribbon. The principal differences between this technique and previous unsuccessful procedures included: 1) use of a low-oxygen boron nitride crucible, 2) use of a tapered orifice, and 3) addition of 2 at.% Al to the alloy combined with use of a carbon monoxide atmosphere during melt spinning. We believe that carbon monoxide and the aluminum form an Al_2O_3 skin on the molten alloy jet that stabilizes it against Rayleigh-Taylor instability.

The yield strain of the ribbon was about 2%, based on a short-time bend test; the yield stress was 3.5 GPa, based on the Vicker's microhardness of $1140 \pm 20 \text{ kg}\cdot\text{mm}^{-2}$. The ribbon showed good ductility, but failure in bending was asymmetric, depending on whether the quench-wheel side was under tension or under compression. X-ray diffraction showed no crystallinity; calorimetric measurements will be made shortly.

Explosive compaction of ceramic powders†

We are investigating the production of ceramic objects by the explosive compaction of aluminum nitride powders. Most nitrides and carbides (e.g., AlN, SiN, SiC, etc) offer outstanding strengths but are difficult to fabricate into shapes useful in engineering applications. Explosive compaction may prove an alternative to sintering as a fabrication process.

Our study is divided into three general areas: fabrication, characterization, and modeling. Work in these areas is proceeding concurrently.

Fabrication

We have analyzed the chemistry, structure, morphology, and particle size of AlN powders on hand. These starting materials contain about 93% AlN, 5% alumina, and 2% aluminum metal. No "high purity" (99+% AlN) material is commercially available, and to date we have not tried to synthesize high purity powders. The AlN powders are stored and handled in a dry box under dry nitrogen to minimize contamination with air and water.

Two approaches for compacting AlN powders are being pursued: implosion using high explosives (HE) and compaction of disks using projectiles fired from high-pressure gas guns. The first approach is being followed to produce crack-free materials that can be used in characterization studies. Previous work by Hoenig and Yust¹⁷ showed that AlN can be compressed to high density using this technique, although the samples were extensively cracked, particularly near the center. At present, four mild-steel capsules ($1.27 \times 15 \text{ cm}$) have been loaded with AlN powder and centered in a 5-cm-diam PVC pipe containing 350 g of HE; they are being degassed and are scheduled to be compacted soon. We will attempt to compact them at nominal pressures of 5, 4, 3, and 2 GPa in order to narrow the "window" of pressures at which the powders are neither under- nor over-compressed. Hoenig and Yust found that 7.5 GPa was excessive, resulting in cracking and perhaps melting at the cylinder axis; at 3.5 GPa, the material at the periphery was well densified but the center appeared under-compressed.

Explosive compaction of a cylindrical capsule of powder has a serious drawback, however; the converging shock wave and its concomitant effects threaten the mechanical integrity of the sample and introduce

*For more information, contact R. W. Hopper (415-422-8001).

†For more information, contact W. H. Gourdin (415-422-8241).

radial variations in the microstructure. Though these effects can be mitigated by matching shock dissipation to the rate of convergence, the proper shock pressure for a given initial powder density must be known. From both theoretical and practical standpoints, it is best to eliminate the convergence problem by compressing in a planar geometry. Although this can be done using HE, it is more advantageous to use projectiles fired from high-pressure gas guns because the impact velocity (and hence the pressure) can be closely measured and controlled. However, because the pressure release from the impact of a projectile is more abrupt than that from a HE-generated shock wave, the shock must be attenuated in some way after it has passed through the compacted material because ceramics have very little tensile strength.

Our initial design for compaction experiments in the gas gun is simple. The AlN powder is held in place in the compaction chamber by a thin plate made of the same material as the projectile. When the projectile is shot from the gun barrel into the compaction chamber, it acts as the moving punch in a punch-and-die arrangement. The AlN powder charge is thick enough to serve as a shock absorber, so that after the projectile strikes the front face, the shock waves attenuate in the powder, and the rarefaction waves reflected from the rear of the die are negligible. Although the density of the compressed powder decreases with increasing distance from the front face, a portion is presumably highly compressed. This experiment will provide information about the thickness of powder that can be effectively compacted and the rate at which the shock wave attenuates.

Characterization

Transmission electron microscopy (TEM) examination of materials previously compacted by Hoenig and Yust using HE showed extensive lattice damage and a very high dislocation density. The deformation appeared to be uniform, which indicated that AlN behaves plastically during compaction. We observed an unusual mottled material at what seemed to be grain boundaries; bright field-dark field analysis indicated that the material is crystalline rather than amorphous, as suggested by Hoenig and Yust. There was some indication of thin layers of a second phase at some grain boundaries, which was not surprising since the starting powders contained several percent alumina. The grains themselves, though often difficult to discern, were 1 μm or less. The compacted material was too greatly deformed to allow an analysis of the microstructure (e.g., slip systems, presence of twinning, fracturing, grain size, and morphology); we are planning annealing studies to remove some defects and simplify the structure.

Modeling

We have attempted to model both types of compaction. We used the hydrocode KO to examine one-dimensional shock compaction using projectiles and the two-dimensional hydrocode HULL to model the HE compaction of powders in a cylindrical geometry.

To use KO, a reasonable equation of state and a high-rate compaction model for AlN were needed. Efforts to obtain these were hampered by the lack of knowledge of the shock behavior of AlN. However, on the assumption that all ceramic powders react to shock similarly (at least in the early stages), a crude Hugoniot based largely on the response of porous alumina was constructed.¹⁸ Complete densification of the AlN was assumed to occur at about 10 GPa. To date, this code has not produced physically reasonable results, and we are working to improve the model.

For the preliminary calculations using HULL, sand was the compacted material and the conditions were chosen to match approximately those used by Hoenig and Kuhl¹⁹ for their shots with AlN. The results were very encouraging. The HULL code was able to handle the converging shock and the singularity at the axis of the cylinder. The calculated results clearly showed the conical compaction front propagating along the axis. The release-wave structure appeared quantitatively similar to that seen in flash x-ray photographs. Not surprisingly, the calculated pressures at the center of the cylinder were extremely high (about 50 GPa).

Sintering of covalent solids*

Most metallic and nonmetallic fine powders can be sintered to near theoretical density when heated close to their melting points. One group of solids, however, cannot be densified by the conventional sintering

*For more information, contact J. B. Holt (415-422-8003).

processes, i.e., without using high pressures or adding impurities. This group includes such technologically important solids as Si_3N_4 , B_4C , SiC , AlN , Si , and Ge ; all of these materials are covalently bonded. Several hypotheses that involve both kinetic and thermodynamic factors have been suggested to explain their non-sinterability, but the underlying cause of this peculiar behavior remains unclear.

We selected Ge as a model system to investigate the non-sinterability of covalent solids, primarily because 1) we are currently measuring the surface diffusion of Ge in our laboratory, 2) we have well-characterized single crystals, and 3) a wide range of physical-property data have already been documented.

In our initial work, we sintered Ge spheres (100–250 μm in diam) to single-crystal Ge plates to measure the rate of neck growth at different temperatures.² These experiments indicated that surface diffusion is the principal mechanism for neck formation; bulk diffusion contributes very little. We also observed that necks formed in argon were nearly round whereas those grown in vacuum were irregular and much larger.

During the last reporting period, we examined the cross sections of several spheres sintered to Ge plates to determine whether the grain boundary at the interface had migrated into the sphere during sintering. Unfortunately, most of the necks fractured as the metallographic mount was prepared, and our results to date have been inconclusive.

We also studied the sintering of Ge powders that were prepared by crushing single Ge crystals in a ball mill and leaching the powders to remove iron introduced by the steel balls. After leaching, the powder still contained 2000 ppm iron. The surface area of the powder was 3.8 m^2/g ; the average particle size was 2 μm , and all particles were less than 20 μm .

Several sintering runs were carried out in argon to determine if the pellets would shrink. The runs included one pellet doped with 0.1 wt% boron, which has been shown to enhance the sintering of silicon.²⁰ After heating the pellets at 850°C for 6 h, none of them had shrunk. However, because the large quantity of iron still present in the powder may have compromised these results, we are preparing a new sample of Ge powder in the Trost mill, which uses the powder itself as the grinding agent and requires no steel balls. We plan to measure both pellet shrinkage (if any) and surface area as functions of time at different temperatures.

Materials Research notes

Hydrogen compatibility of stainless steel*

During the past year, we have studied the hydrogen compatibility of two warm-worked high-strength stainless steels: 21Cr-6Ni-9Mn and Type 316. We are investigating the influence of yield strength on the fracture mode of stainless steel tubing that is exposed to hydrogen at high pressure. This tubing is a candidate material for use in high-pressure hydrogen-containment vessels. We have previously reported mechanical property data obtained from these studies.²

Our recent experiments revealed a new phenomenon that is not presently understood. When 316 stainless steel is subjected to hydrogen gas at 69 MPa, the yield strength increases from 807 to 910 MPa and the fracture mode changes from ductile dimple to a brittle fracture. Although the presence of hydrogen reduces K_Q (the apparent fracture-toughness parameter) by only about 10%, we considered the change in fracture mode more disturbing because brittle fracture can occur without warning (i.e., no prior plastic deformation). Experiments at Sandia National Laboratories showed that when special higher-strength 316 stainless steel was tested at an initial stress-intensity factor of $132 \text{ N}\cdot\text{m}^{-3/2}$, cracks did grow slowly within 1300 h whereas no cracks formed at $88 \text{ N}\cdot\text{m}^{-3/2}$. When these $K_{\text{threshold}}$ data are plotted as a function of yield strength, the results are consistent with data obtained for several other austenitic steels.

It may be simply fortuitous that the yield strength of our high-pressure stainless steel tubing is less than 759 MPa and that we have not observed any brittle fracture or slow crack growth when this tubing is subjected to high-pressure hydrogen.

Cyclone design for collection of aerosol flyash particulates†

We are analyzing the collection efficiency of three cyclone designs, one of which will be used in a proposed high-volume sampler (200 cfm) that fractionates (by size) and collects power-plant stack aerosols. To fractionate these particles aerodynamically, this sampler must include three or four cyclone collectors arranged in series and followed by an electrostatic precipitator and filter.

During this reporting period, we calculated the particle distributions that would be collected by the three cyclone systems on the basis of several simulated input aerosol distributions. We compared our calculated results to those obtained by the 40-cfm sampler at the University of California at Davis. This work is sponsored by DOE through the Environmental Sciences Division at LLNL.

We considered the following cyclone configurations; each cyclone in the series captures 50% by number of the particles of the size listed:

1. 10, 5, 2.5 μm .
2. 10, 2.5, 1.2 μm .
3. 10, 5, 2.5, 1.2 μm .

The third configuration included four cyclones.

The collection efficiency ϵ for a given cyclone collector is a function of the particle radius r and can be expressed as

$$\epsilon(r) = 1 - e^{-\alpha r}, \quad (14)$$

where α is a constant for any given cyclone.

*For more information, contact P. R. Landon (415-422-7063).

†For more information, contact A. H. Biermann (415-422-8017).

We simulated the amount of material collected by the cyclone train by assuming a log-normal size distribution as the input for the first cyclone. The amount of material retained by the first cyclone was calculated by multiplying the efficiency ϵ given by Eq. (14) by the number of particles of radius r :

$$n_{c1}(r) = n(r)\epsilon_1(r) \quad (15)$$

where

n_{c1} = number of particles of size r collected by cyclone 1,

n = input size distribution,

ϵ_1 = efficiency of cyclone 1 for size r .

This statistical treatment is extended for the subsequent cyclone collectors.

We tested three input size distributions. The different distribution spreads corresponded to standard deviations of 2.00, 2.25, and 2.50 around a nonparametric-mass median diameter of $1.0 \mu\text{m}$ (Fig. 17). The calculated size distributions and amounts collected for each of the cyclone configurations were compared to a sample collected by the U. C. Davis sampler (Table 6). We concluded that our most conservative design (No. 1) should perform as well as the U. C. Davis sampler in collecting stack aerosols.

Fig. 17. The different distribution spreads corresponding to standard deviations of 2.00, 2.25, and 2.50 around a nonparametric-mass median diameter of $1.0 \mu\text{m}$.

Table 6. Comparison of collection efficiencies and size distributions of particles collected by the University of California at Davis sampler and our (10, 5, 2.5) cyclone configuration.

Stage	U.C. Davis sampler		(10, 5, 2.5) cyclone configuration	
	efficiency (%)	m ₅₀ (μm)	efficiency (%)	m ₅₀ (μm)
1	66.6	20	57.5	18
2	16.2	6.3	26.6	9
3	7.3	3.2	11.1	6
4	9.9	2.2	4.7	3

Presentations

S. A. Brawer	Monte Carlo Simulation of Eu-doped BeF ₂ Glass.	Invited talk. Argonne National Laboratory, Argonne, IL, May 1980
S. A. Brawer	Monte Carlo Simulation of Rare-earth-doped BeF ₂ Glass	Invited talk. American Physical Society, New York, NY, March 1980
S. A. Brawer	Relation Between Structure and Spectroscopy for Monte-Carlo-simulated Rare-earth-doped BeF ₂ Glass	Invited talk. American Ceramic Society, Chicago, IL, May 1980
R. D. McCright R. Quong	Corrosion Testing at the Salton Sea Geothermal Site	LLNL Associate Director's Review of Energy Programs, Livermore, CA, April 18, 1980
R. D. McCright	Status of LLL Materials Testing Work	DOE Headquarters, Washington, DC, May 22, 1980
R. D. McCright	Recommendations for Future Geothermal Corrosion Evaluation Programs	DOE Headquarters, Washington, DC, May 22, 1980
R. M. Scanlan	High Field Superconducting Magnet Development at LLL	Workshop on High Field Superconductors, Tokyo, Japan, March 13-15, 1980
Gordon S. Smith	X-Ray Diffraction Studies of SYNROC Waste Forms	82nd Annual Meeting and Exposition of the American Ceramic Society, Chicago, IL, April 1980

Publications

S. A. Brawer	Studying Glass Structure with Laser-Excited Fluorescence and Computer Simulation April 1980	<i>Energy and Technology Review</i> , April 1980
S. A. Brawer	The Glass Transition in BeF ₂ : A Monte Carlo Study	<i>J. Chem. Phys.</i> 72 , 4264 (1980)
L. D. Calvert, J. L. Flippen-Anderson C. R. Hubbard Q. C. Johnson P. G. Lenhert M. C. Nichols W. Parrish D. K. Smith G. S. Smith R. L. Snyder R. A. Young	Standards for the Publication of Powder Patterns: The American Crystallographic Association Subcommittee's Final Report	National Bureau of Standards Special Publication 567. Proceedings of Symposium on Accuracy in Powder Diffraction, held at NBS, Gaithersburg, MD, June 11-15, 1979
J. E. Harrar F. E. Locke C. H. Otto, Jr. L. E. Lorensen W. P. Frey E. O. Snell	On-Line Tests of Organic Additives for the Inhibition of the Precipitation of Silica from Hypersaline Geothermal Brine IV. Final Tests of Candidate Additives	UCID 18536
J. E. Harrar F. E. Locke C. H. Otto, Jr. S. B. Deutscher W. P. Frey L. E. Lorensen E. O. Snell R. Lim R. W. Ryon R. Quong	Final Report on Tests of Proprietary Chemical Additives as Antiscalants for Hypersaline Geothermal Brine	UCID 18521
R. L. Landingham A. W. Casey A. R. Ulrich	Examination of Shiva Bedment Bolts Which Failed during the January 24, 1980 Earthquake	UCIR 1358
R. D. McCright	LLL Industrial Support Program Test Results on Scale Control, Corrosion, H ₂ S Abatement, and Injection at the Salton Sea Geothermal Field	UCID-18596
R. D. McCright R. A. van Konynenburg	Radiation Effects on Tube Denting in the Steam Generators of Pressurized Water Reactors	UCRL-52892

R. D. McCright

Post Closure and Retrieval Considerations of Spent Fuel and Transuranic Waste Disposal in Salt

UCRL 84208

R. J. Morgan

E. T. Mones

W. J. Steele

S. B. Deutscher

The Structure and Property Relationships of Poly (p-Phenylene Terephthalamide) Fibers

UCRL 84208

Preprint

Gordon S. Smith

Advances in the Computer Indexing of Powder Patterns

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